

Correlation of Coal Quality to Coal Liquefaction

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Introduction

A large-scale direct coal liquefaction plant will consume substantial quantities of coal as a feedstock material. Due to the nature of the coal mining industry this supply will be acquired from several mines operating in different coal reserves. Procurement of coal from multiple sources, over time will undoubtedly lead to variations in the characteristics of the plant feed. Physical and chemical coal properties are known to vary within a reserve due to the mechanisms of seam formation and subsequent geologic metamorphism. In addition, mining methods and physical beneficiation affect the organic and inorganic constituents in the mine product. Furthermore, the specification of a single seam, for example Ky #9 or Ill. #6 as the source for potential feed-coals, is insufficient since it has been shown that substantial variations in coal properties can exist within a single seam.

Although it is clear that variations in feed coal properties can affect plant operations and yields, few quantitative relationships have been developed. The difficulty in understanding the importance of coal characteristics is in part related to the complex nature of coal, and problems in the selection, characterization and testing of representative feedstock samples. The driving force for developing this understanding is directly related to the selection and procurement of the essential raw material for liquefaction processing. A scientifically based understanding of how to select coal sources from within a mining region and how to compensate for variations from an individual mine will improve the operability and economics of any direct liquefaction plant.

This study has investigated the degree to which coal properties change within a supply region and how these variations impact on yields and economics of an SRC-I type process. Statistical data analysis has isolated critical coal properties influencing liquefaction reactivity and quantitative prediction equations have been developed.

General Coal Characteristics Influencing Reactivity

Research work to identify the suitability of U.S. Coals for direct liquefaction were begun by the U.S. Bureau of Mines station at Bruceton, PA in the early 1940's^{1,2}. These efforts investigated coals of varying petrographic composition and rank, concluding that these characteristics significantly affected the ease by which a coal could be liquefied. More recently, work has been completed by a number of investigators which confirms that the total reactive maceral content of the coal is related directly to its overall conversion to extractable products^{3,4,5}.

Although coal rank is recognized as a derived property related directly to a coal's composite organic chemical structure, its impact on liquefaction reactivity is not clearly understood. Most researchers are in agreement that coals higher in rank than high volatile A bituminous are poor candidates for liquefaction feedstocks due to low reactivity. This limitation presents little problem for the development of a coal liquefaction industry since these high rank coals represent only ten percent of the country's production. The

more abundant lower rank coals have displayed divergent reactivities depending upon the experimental conditions and method of investigation. Neavel⁷ has shown that the coal conversion to benzene solubles plus gases is inversely proportional to the rank of the coal for residence times from 2.5⁶ to 30 minutes. These results are generally in agreement with those of Whitehurst⁸ and Yarzab⁹ for long residence times. However, Whitehurst⁸ has shown that in short residence time coal liquefaction, low rank coals are substantially less reactive than high volatile bituminous coals of similar petrographic composition. In processing coals under SRC-II conditions using disposable iron catalysts, Wright¹⁰ has found that lignites and subbituminous coals have higher conversions and greater yields of distillate than high volatile bituminous Pittsburgh Seam coals. Thus, providing that reaction conditions are chosen correctly, the coal is prepared properly prior to liquefaction and sufficient catalyst is present, lower rank coals would appear to have higher reactivity than high volatile bituminous coals.

One coal characteristic not explained by measures of rank and petrographic composition is the nature of inherent mineral matter. Many authors have shown that mineral matter in coal can act as an inherent catalyst for improving liquefaction yields. The consensus of this work has been that iron sulfides, particularly pyrite,⁹ are the most effective catalysts present in the inherent coal mineral matter.¹⁰ Although some differences in pyrite catalysis activity have been reported,¹⁰ most work has shown that the very high levels (up to 10% pyrite on coal) must be added to affect a significant change in the yield structure of Eastern Bituminous Coals.^{11,12} Low iron subbituminous coals can be made more reactive with somewhat lower levels of pyrite addition.¹³

Experimental Investigation of Coal Reactivity

The International Coal Refining Company (ICRC) Research Group has been heavily involved with developing experimental data to support the SRC-I Demonstration Plant Project. A portion of this effort was to determine the effects of feed coal variation on plant performance. Although the majority of potential feed coals for this plant would come from a restricted area (Illinois Basin), it became clear in this program that three major technical areas would need investigation as follows:

- o Coal variation from an individual mine,
- o Coal variation within the reserve area, and
- o Effects of these variations on liquefaction yields.

Due to design and operation considerations, a decision was made early in the demonstration plant program to consider only use of washed coals. This constraint significantly limited the number of mine operations which could be considered as suppliers.

An experimental program was established with the Institute of Mining and Minerals Research, University of Kentucky, to sample mining operations in a pattern to provide geographic and stratigraphic diversity. The sample locations, in relation to the mining regions are shown in Figure 1. Samples were collected from the run-of-mine coal as well as the washed coal. Several mining operations were studied for both long- and short-term variation in coal properties.

In the short term coal variability study, samples were collected from the operation daily and analyzed for changes in composition. Figure 2 shows the daily shifts in sulfur and ash content for a mine in the KY #9 seam. These results demonstrate that the coal cleaning plant is necessary not only to

reduce the amount of mineral matter in the coal, but also to buffer variations in composition due to mining. An additional benefit from coal preparation is an increase of approximately three percent in the total reactive maceral content of the clean coal, enhancing the liquefaction potential.

Based upon the results from the short term study, a five day period was selected as the time in which to composite a sample to define a plant's average output. Thus, once a month a five day period was sampled and composited for each of six months. These results (Figure 3) show that some long term shifts in clean coal composition can occur. The variations may result from changing characteristics of an individual coal reserve or changes in mine operations. A liquefaction processing plant will need the flexibility to deal with these changes if they would significantly affect operations.

The second portion of this project was to define the regional variation in coal composition. Table 1 shows the range in several clean coal properties across the region compared to the variation which might be expected from an individual plant. These results illustrate that the variation across the region is generally two to four times that which might be expected from an individual plant. Furthermore, the absolute ranges in variables, such as vitrinite reflectance, pyritic sulfur and total reactive macerals, are such that they will affect substantially coal liquefaction results. Therefore, despite the contention that coal supply from an individual mine will shift with time, there are probable advantages to selecting and blending coals from mines whose average composition is in the high reactivity range.

The third portion of this program was to test the set of clean coals to determine the effects of variations in properties on coal liquefaction. In this program the coals were liquefied in a 100 pound per day continuous bench scale process development unit (CPDU) under standard conditions as follows:

o Reaction Temperature	840°F
o Reaction Time	30 min
o Total Pressure	2000 psig
o H ₂ Flow Rate	28,000 SCF/Ton Coal
o Coal Concentration	40 wt.% in Wilsonville Recycle Solvent

These are essentially the SRC-I standard process conditions with the exception of the shorter (30 min) residence time. All samples from the process unit were analyzed by a standard workup procedure to determine the yields of products on a dry ash-free coal basis and hydrogen consumption.

Figure 4 shows the range in reactivity demonstrated by these coals as related to oils yield and hydrogen consumption. These two factors are useful for assessing coal reactivity since they are among the most sensitive economic parameters in a liquefaction plant. The results show a group of high reactivity coals (>25% oils yield), a group of average coals (15-25% oils yield), and one very low activity sample.

Ranges in coal reactivity of this magnitude impact both on plant operations and on revenue economics. Improvements to plant operation may include: improved solvent balance, less loss of preasphaltenes to the gasifier residue, and the flexibility to operate at lower severity. The advantages of operation at a decreased severity are lower duty on the fired preheater and better reaction stability. Of course, to operate with a high reactivity coal at high severity would require some additional hydrogen capacity and this element does impact on operations and economics.

Table 2 shows a yield and economic comparison of operating a hypothetical single-stage SRC-I type plant in a maximum heavy fuel oil mode. This analysis assumes that all the middle oil produced will be blended with the solid SRC and sold as heavy oil. The comparisons are shown on an identical plant case, operating with an average and, alternatively, a high activity coal. Although this assessment has been simplified and contains several assumptions, it is clear that using the high activity coal, including the hydrogen penalty, results in a significant (11%) improvement in revenues. Since these coals are sold currently on a fuel basis (cents/mm btu) there can be compelling economic incentives for choosing high activity coals.

The advantages in operations and economics for a simple thermal process (i.e. SRC-I) also appear to be present for more complex catalytic systems. Figure 5 shows the results of processing a low activity and a high activity coal, with and without a slurry phase catalyst. In this comparison, it is evident that the catalyst acts to provide an incremental improvement in oil yield over the baseline non-catalyst case. Rather than seeing the yield structures converge due to catalytic processing, they maintain approximately the same differential as the original coal reactivity. Although these results demonstrate that initial coal activity dominates in one stage thermal and catalytic processes, it is not clear what impact it has on integrated two-stage processing.

Analysis of Liquefaction Data

In order to realize an advantage due to coal reactivity in either operations or economics, it is necessary to understand methods of selecting high activity coals. One objective of this research program was to develop correlations between coal characteristics and liquefaction product yields. In order to develop these types of correlations it is necessary to have a homogeneous data set which provides a sufficiently broad, and normally distributed, pattern of variables. Although the current dataset is probably too small (13 coals) to develop highly correlated relationships, it is useful for determining trends in the data.

The coal characteristics and liquefaction yield data sets were both analyzed to detect and minimize strong statistical intercorrelations. This analysis resulted in the selection of four independent coal variables and five relatively independent liquefaction variables which were correlated against each other (Table 3). Based on the relationships detected from Table 3 the following empirical prediction models were calculated.

$$\text{Total Conversion} = (14.1 \text{ (Pyritic Sulfur)} + 4.1 \text{ (Vitrinite reflectance)} + 77.2) \times \text{Total Reactive Macerals}/100 \quad \text{Eq. 1}$$

$$R^2 = 0.82$$

$$\text{Oil Yield} = 16.2 \text{ (Pyritic Sulfur)} - 1.2 \text{ (Volatile Matter)} + 13.6 \text{ (Vitrinite Reflectance)} + 52.9 \quad \text{Eq. 2}$$

$$R^2 = 0.47$$

The multiple R-squared for equation #1 (0.82) is relatively good for complex multivariate relationships such as those existing in coal research. The constant term in this equation (77.2) is relatively large in comparison to

the values of the predicted variable and attempts to generate a strong relationship would work to reduce this value. The parity plot in Figure 6 of the observed conversion versus the predicted conversion shows there are no significant outliers (or large residuals) in this data set and that predictive relationship is reliable. Unfortunately, the R-squared for equation #2 is not as good (0.47). Figure 7 is the parity plot of oil yield observed versus oil yield predicted for this equation; it indicates that there are no single or patterned outliers. This suggests that an additional characterization factor is probably necessary to improve the prediction of oil yield.

This analysis of the data set resulted in the selecting of many of the same variables as those determined by the Pittsburgh & Midway Coal Mining Co. for the prediction of SRC-II yield structures. The relationship between pyritic sulfur in the clean coal and the conversion of total reactive macerals detected in the statistical analysis (correlation coefficient equals 0.902) is shown in Figure 8. This relationship shows that as pyritic sulfur drops below 1.10 wt. percent, the coal conversion reactivity decreases significantly. However, in another portion of the research program, experiments on the importance of coal preparation showed that levels of pyritic sulfur had little effect on liquefaction yields. The results from one of these experiments are shown in Figure 9. Despite coal samples which range in ash and pyritic sulfur in excess of those detected in the data analysis, the liquefaction yields are rather consistent.

The reconciliation of these seemingly diametrically opposed results appears to reside in the activity of the pyrite present in cleaned coals versus that in the run-of-mine and partially cleaned samples. A series of coals all cleaned to approximately the same ash level would be expected to contain approximately the same amount of pyrite, if it were distributed in the same manner in all the samples. The cleaned coals in the data analysis set (similar in preparation and ash content) ranged in pyritic sulfur from 1.42 to 0.65 percent, indicating that some of the samples probably contained pyrite which was finely dispersed in the organic matrix and was not removed by cleaning. Generally, these coals were those which had high activity for liquefaction. The pyrite that would be present in the level 1 and level 2 cleaning shown in Figure 9 would be comprised substantially of coarse material from seam partings and pyrite nodules. The experimental data on these samples indicate that this type of pyrite has little catalytic effect in the SRC-I liquefaction system. The majority of the catalytic activity appears to be provided by the finely dispersed pyrite retained in certain cleaned coals.

The importance of pyrite dispersion is also in general agreement with results determined in the disposable catalyst programs.^{11,12,15} These workers found that additions of particulate pyrite at levels approaching 5 weight percent pyritic sulfur on coal were necessary to show much catalytic activity. However, when iron was added to the coal in a dispersed system, much lower levels resulted in high catalytic activity.¹⁶ Hence, not only the amount, but more importantly the form of the pyrite in the coal appears to be the most important factor in controlling its contribution to the coal activity.

One can conclude also from the data analysis that the level of geochemical maturity, or rank of the coal as measured by vitrinite reflectance, is of significance to liquefaction yields. Although the range of rank in these samples is not as large as might be necessary to fully identify this effect, increases in rank correlate negatively with both oil yield and conversion. The subtle differences in the ranks of the coals in this sample suite do reflect changes in the structural chemistry of the coal macerals. In this range of geochemical maturity, coals lose oxygen and are believed to undergo

rearrangement and ring condensation. These reactions may tend to result in a more refractory organic phase to dissolution and liquefaction. A negative correlation of liquid yield and conversion with coal rank parameters was also reported by the P&M workers.

Summary

It is clear from the preceding discussion that variations in coal properties do affect liquefaction results. The observed differences between coals can be as large as those between Western Subbituminous compared to Eastern Bituminous, or as small as changes in coal within a single seam or individual mine. These variations in properties do affect liquefaction yields, plant operations and economics. Selection of coals, even from a restricted region, can be advantageous since critical properties vary more from source to source than from an individual mining operation.

Research at ICRC and elsewhere has shown that quantitative relationships can be developed between coal characteristics and yields. These efforts have shown that the amount of dispersed pyrite in the coal, the geochemical maturity and the petrographic composition are important coal parameters. Clean coals from this region with less than 1.10 wt. percent pyritic sulfur were found to have significantly reduced liquefaction reactivity. Unfortunately, the prediction of oil yield from coal properties has proven difficult and will probably require the addition of more fundamental parameters of coal chemistry to improve its precision.

An improved understanding of the relationship of coal properties to liquefaction results would be useful from a scientific point of view as well as a processing standpoint. The advantages of selecting and manipulating coals for improved processing results are self evident. The impact of pyrite dispersion in the organic matrix may indicate that initial dissolution reaction and associated hydrogen rearrangement, promoted by an in-situ catalyst, are instrumental in defining the final product distribution. The ability to better understand the mechanisms of coal dissolution from a fundamental point of view may lead to new improved processing concepts, as well as a better understanding of the U.S. coal resource.

Acknowledgement

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TABLE 1
COAL CHARACTERISTICS VARIATION IN SUPPLY REGION

	MEAN	VARIABILITY*	COEFFICIENT OF VARIATION	MAXIMUM COEFFICIENT OF VARIATION OF A SINGLE PLANT
ASH	9.2	±4.7	0.25	0.11
HEATING VALUE	12283	±1100	0.09	0.04
TOTAL SULFUR	3.1	±1.3	0.21	0.12
PYRITIC SULFUR	1.4	±1.0	0.36	0.23
T. R. MACERALS	93.3	±3.1	0.02	0.01
VIT REFLECTANCE	0.57	±0.18	0.16	0.04

* ± 2 STANDARD DEVIATION

TABLE 2
YIELD AND ECONOMIC COMPARISON

PRODUCTS	AVERAGE ACTIVITY COAL	HIGH ACTIVITY COAL
	YIELD*	YIELD*
FUEL GAS	4.5	7.4
LIGHT OILS	8.0	12.8
MIDDLE OILS	0.0	0.0
HEAVY OILS	17.5	29.1
SOLID SRC	44.8	27.1
TOTAL PRODUCTS	74.8	76.4
TOTAL REVENUE**	\$ 8.90	\$ 9.88

*LBS OF PRODUCT/100 LBS DAF FEED COAL

**DOLLARS OF REVENUE/100 LBS DAF FEED COAL (1990 PRICES IN 1981 DOLLARS)

TABLE 3
**CORRELATION OF INDEPENDENT COAL CHARACTERISTICS
AND LIQUEFACTION YIELD DATA**

	HYDROGEN CONSUMPTION	HYDROCARBON GASES	TOTAL OILS	CONVERSION OF TRM	ASPHALTENES/ PREASPHALTENES
DAF HYDROGEN	0.176	0.156	0.022	0.103	-0.191
DRY PYRITIC SULFUR	0.661	0.131	0.527	0.902	0.214
DAF VOLATILE MATTER	—	0.283	-0.243	0.121	-0.311
VITRINITE REFLECTANCE	-0.153	-0.289	-0.159	-0.360	-0.120

Figure 1
COAL SAMPLE LOCATION MAP

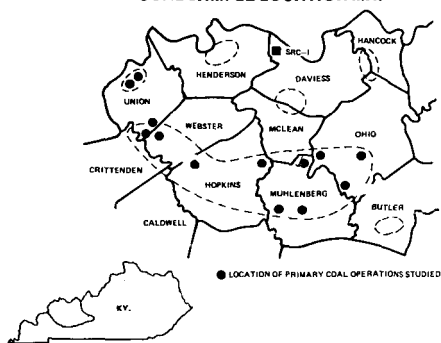


Figure 2
COAL FEED VARIABILITY

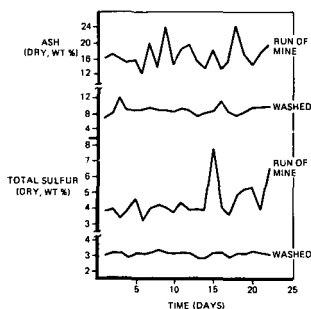


Figure 3
COMPOSITION VARIABILITY
(CLEAN COAL)

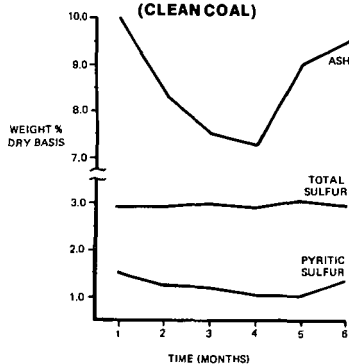


Figure 4
COAL SCREENING PROGRAM

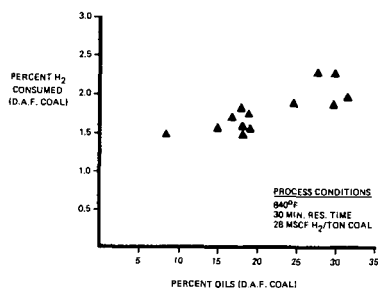


Figure 5
EFFECTS OF SINGLE STAGE
CATALYTIC LIQUEFACTION

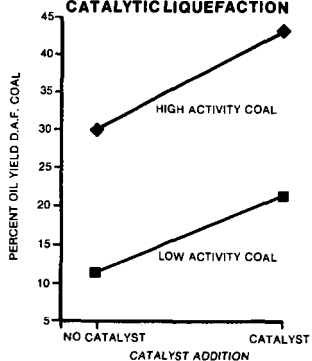


Figure 6
PARITY PLOT - PERCENT CONVERSION OBSERVED VS.
PERCENT CONVERSION PREDICTED

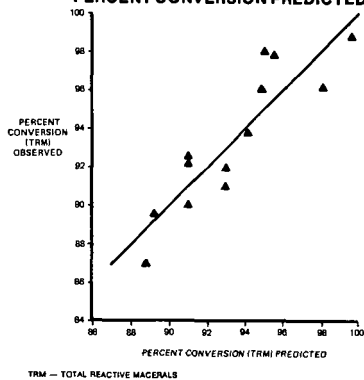


Figure 7
PARITY PLOT - PERCENT OIL YIELD OBSERVED VS.
PERCENT OIL YIELD PREDICTED

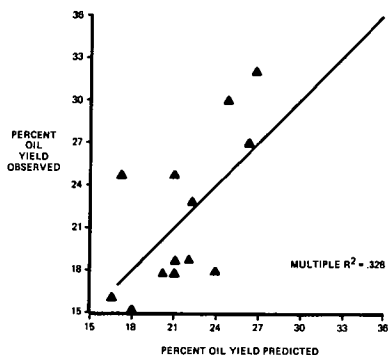


Figure 8
RELATIONSHIP OF PYRITIC SULFUR CONTENT
TO COAL REACTIVITY

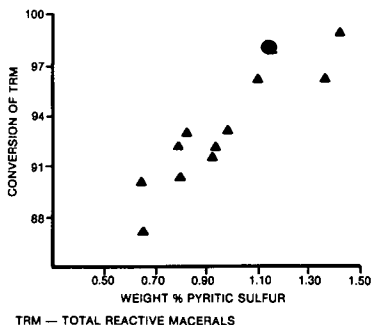
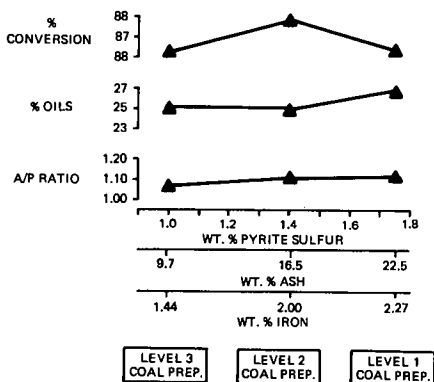


Figure 9
EFFECTS OF COAL CLEANING ON
SRC-I LIQUEFACTION



A/P ASPHALTENE/PREASPHALTENE

Correlation of Recycle Solvent Quality to Coal Liquefaction

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INTRODUCTION

"Solvent quality" is a contrived solvent property used in coal liquefaction. It is assumed to be an important guide for expressing how well a recycle solvent will convert coal to products soluble in tetrahydrofuran (THF) or pyridine. Over the past 40-50 years, much has been written about the solvents used to prepare coal slurries, yet few solvent quality parameters have been quantified and related to process conditions or feedstocks.

For this report, solvent quality was measured by kinetic microautoclave test as used at the Wilsonville Advanced Coal Liquefaction Facility (1). The microautoclave method, originally developed by the Conoco Coal Development Company, has been used to quantify solvent quality at Wilsonville since 1978. This method (Note 1) defines solvent quality as the weight percent tetrahydrofuran solubles generated, based on weight percent moisture- and ash-free (MAF) coal. Traditionally, a solvent quality test result in the lower range (~65) warned of potential preheater coking problems. More recently, solvent quality has been used to monitor the effects of adding light solvent refined coal (LSRC) and distillates to the solvent stream to enhance coal liquefaction and maintain solvent balance.

This study attempts to identify important independent and dependent variables associated with the solvent refining of coal (SRC) by relating plant operation to coal feedstock and product slate and by correlating the impact to changes in the results from the microautoclave solvent quality test.

PROPERTIES AND CHARACTERISTICS OF COAL LIQUEFACTION SOLVENTS

In SRC liquefaction, an effective process solvent should be (a) coal-derived to permit continuous plant operation; (b) a distillate with a nominal boiling range of 450-850°F; (c) able to sustain a 10-40 wt % coal slurry through feed pumps; (d) able to rapidly accept coal dissolution products in solution or suspension; (e) able to act as a hydrogen donor or shuttling agent for hydrogen transfer under a predominantly free-radical mechanism; and (f) capable of carrying the liquefaction product stream through solid/liquid separation processes and ultimately of being recycled to continue the process.

The chemical properties of recycle solvents have been well-documented by Whitehurst et al. (2), Burke et al., (3) and Neavel (4). A recycle solvent generated under SRC-I process conditions exhibits a complex molecular composition. The solvent is composed of a mixture of alkyl (C_1 - C_{14})-substituted polynuclear hetero- and hydroaromatic compounds. Gas chromatography/mass spectrometry (GC/MS) data have revealed that 40 individual components comprise almost 60 wt % of the solvent. The remaining 40 wt % may include hundreds to thousands of individual compounds (5). The major molecular species are (5-30%) substituted naphthalenes and (5-10%) phenanthrenes.

During SRC-I liquefaction, each time the solvent/coal mixture passed through the reactor 0-30 wt% new solvent material is generated, on an MAF feed coal basis. Therefore, the molecular composition would be expected to constantly change and shift in response to processing conditions and feed slurry composition. At Wilsonville, the virgin distillate solvent exits the process at vacuum tower T102, trays 3 and 8 (see Figure 1 for a process flow scheme). The solvent is then held briefly in a holding tank (V178), from which daily samples are taken for solvent quality testing.

Recently, the solvent in V178 (originally V131A) has been mixed with LSRC or other product streams in tank V131B just before it is recycled into the process at V101A as a new coal slurry. The LSRC, a product stream from the critical solvent deasher, is added to the distillate solvent for several reasons. Most important to the overall process is that LSRC appears to enhance solvent quality by adding high-boiling compounds (6), and somehow promotes distillate yield so that solvent balance is maintained. Handling the LSRC in material balance calculations is a problem. If the LSRC is inert, it can simply be subtracted. However, if the LSRC is a reactant, its degree of conversion must be quantified before an oil yield can be computed (7). Because the addition of LSRC to the distillate solvent has not been continuous for all coal types, solvent quality values from V131B samples are not included throughout this report.

Anthracene oil is sometimes added to the system at V178 to maintain solvent balance. For this study, data points were eliminated if more than 5% by volume anthracene oil was added to the V178 solvent within 5 days of a material balance period.

THE ROLE OF SOLVENT IN SRC-I LIQUEFACTION

Our current understanding of coal liquefaction is that bituminous coal, when mixed with solvent at 200-250°F begins to dissolve, but that most of the coal matrix is in suspension. The primary dissolution products are believed to be small molecules already trapped within the coal (8). Depending on coal type and rank, these compounds may represent 5-20% of the coal.

At Wilsonville, the feed slurry is held at 150-250°F (depending on the percent LSRC added) for 8-12 hr without hydrogen before it enters the preheater (B102) under partial hydrogen pressure. Under these holding conditions in tanks V101A and V101B, the recycle solvent must exhibit good dissolving power. That way, the solvent can extract and exchange with the small molecules trapped in the coal and fill other voids created by loss of water and swelling.

Thermal reactions, in which scissile bonds (9) break and initiate actual coal matrix liquefaction, do not occur until ~600°F. Such temperatures are first reached in the preheater (B102) under ~2,000 psi hydrogen pressure. At liquefaction temperatures, the nascent free radicals apparently rapidly combine with labile hydrogen from the feed coal during the first .1-5 min, forming a cresol- (or pyridine-) soluble product (4). When temperatures in the preheater reach 780°F, the recycle solvent appears to rapidly solvate the primary liquefaction product. After the process slurry stream enters the reactor, the exothermic reaction drives the temperature to almost 840°F during a residence time of 30-60 min. In the reactor the original recycle solvent and the new coal product components shuttle hydrogen to free-radical sites generated from splitting and cracking at reaction temperature (840°F).

The solvent, which is now modified in molecular composition by the addition of cracking and splitting products from 0-30 wt % MAF coal, can itself be rehydrogenated. This newly available, "donatable" hydrogen can be shuttled to more recently generated active sites formed in reactor R101 to further stabilize the system.

That portion of the solvent that is active in shuttling hydrogen to free-radical sites has been associated with the hydroaromatic content. Other hydrogen-transfer species have been suggested (2) to be active when hydroaromatic species were absent or depleted, including aromatic hydroxyl (e.g., β -naphthol) and alkyl (methyl) side chains like those found on 2-methylnaphthalene. Curran et al. (10) concluded that the liquefaction solvent needs sufficient donatable hydrogen to promote greater distillate yield and reduce coking, and that the hydrogen can come from many sources.

Correlation of Solvent Quality to Process Operation

A review of past operating reports from Wilsonville and interviews with Wilsonville staff resulted in an assemblage of 48 primary parameters that define a pilot plant run under the SRC-I first-stage regime (Note 2). Fifty-seven data points analyzed for these 48 variables span from 1978 (run 133) to 1982 (run 234). During this period, five major coal types were processed for 3-58 days on stream, per run. Usually one to three data points from each run were selected to represent a material balance at nominal steady-state conditions. These material balance points form the data base of this report.

In analyzing these data, we assumed that each coal type can be viewed independently, and that data for each coal type can be averaged. The reason for this assumption was that we believe the variability in coal reactivity changes the demand on the operating conditions, generates a coal-specific recycle solvent after line out, and would promote a unique product distribution. All coals or similar coal types are combined only when deemed necessary for general comparison purposes. The objective of this study is therefore to relate the microautoclave solvent quality test result to process factors that cause or are affected by a change in the solvent's role in SRC-I liquefaction.

The objectives of first-stage SRC-I liquefaction are assumed to be:

- o Maximum conversion of coal to cresol (or pyridine) solubles
- o Minimum hydrogen consumption based on MAF coal conversion
- o Maintenance of process solvent in solvent balance
- o Minimum hydrocarbon and maximum heteroatom gas production
- o Minimum preasphaltenes content in the vacuum tower (T102) bottoms

The major process variables considered are coal type, dissolver (R101) temperature and pressure, and coal space rate in the dissolver.

Reaction severity, i.e., the degree of coal conversion to distillate and gas, can be assessed from yield structure information, such as hydrocarbon and heteroatom gas production (total gas minus H_2O) and net hydrogen consumption.

Although total gas production may not seem to relate to the recycle solvent's physical or chemical properties, it is presumed to be affected by "solvent quality." Solvent quality in this case refers to the solvent's ability to shuttle hydrogen to those coal species that have split into large components and to minimize hydrocarbon cracking that forms C_1 - C_4 gases.

The benzene solubles (SRC oils and asphaltenes) of the vacuum tower bottoms (T102) and the total SRC (pyridine solubles) of this same stream may be the best analyzed samples to quantify both product distribution and reaction severity. This T102 bottoms stream is "process-normalized" in that minor process excursions are averaged by the volume and throughput of the tower.

Process solvent is not measured, but it is determined by difference when calculating a material balance from laboratory distillation (450-end point) and subsequent gas chromatography results (450-850°F). We believe process solvent yield is neither a precise nor an accurate parameter to consider for correlation.

The light oils (C_5 -450°F), which are quantified by gas chromatography data, provide another measure of liquefaction severity and solvent breakdown independent of total gas production.

Table 1 lists typical process parameters with the limits of the values accepted as equivalent in this study.

Table 1

Wilsonville SRC Process Conditions

Dissolver pressure	1,700 \pm 100 psig
Dissolver temperature	825 \pm 10°F
Dissolver volume in use	75%
Coal space rate	38 \pm 3 lb/hr-ft ³
H ₂ partial pressure (heater inlet)	1,470 \pm 75 psi

Representative solvent quality test results for V178 (holding tank) solvent collected over the past 4 years are plotted as a function of time and coal type in Figure 2. Day-to-day variation can be as great as 10 units on the solvent quality scale. As an analytical test, solvent quality may be considered to have a precision of ± 2 .

RESULTS

Total Gas Production

Figure 3 plots the entire data set for total hydrocarbon and heteroatom gas production (MAF coal) vs. solvent quality for all coals. The distribution is clustered at $8 \pm 2\%$ total gas and 75 ± 6 solvent quality. Replotting total gas production from Kentucky #9 coal only gives four distribution curves, one for each mine. Figure 4 shows that each plot has distinct clusters and a few outlying data points. In Figure 4, the data points are coded to define common dissolver conditions (pressure, temperature, and volume used). Only in the Fies Mine Kentucky #9 coal is there an apparent shift to greater gas production at higher dissolver temperature and pressure. Figure 5 provides a different perspective by plotting total gas production data as a function of days on stream over 4 years. Note that because all data points are presented, process conditions varied more than the accepted limits given in (Table 1) for any one common preheater/reactor condition. Note that high gas production usually follows a change in coal type. This trend is apparently independent of reactor pressure, coal space rate, and almost independent of temperature (825-840°F).

Gas production is graphed as a function of total elemental hydrogen consumption in Figure 6; all data points are presented. If a total gas production range of 5-10% and a hydrogen consumption of 1.5-3% on MAF coal are arbitrarily set as lower and upper limits, the points outside these limits are mainly those from the material balance periods taken within 30 days after a change in coal type for SRC-I processing. These same points are the outlying data points in Figure 4.

Product Correlation to Solvent Quality

In order to analyze the data meaningfully and objectively, we related solvent qualities to product distribution by coal type at the selected material balance periods. Process variables such as preheater temperature and reactor pressure, temperature, and volume are documented in the discussion.

Dotiki Kentucky #9 Coal. The major differences in processing Dotiki coal occurred between Runs 202/203 and 204/206/208. The first set of runs was conducted at a lower dissolver temperature (825 vs. 840°F). Also, the pyrite content of the coal in runs 206B and 208 was less than 1.1%, whereas in run 203 it was 1.3%.

Figures 7A-7D plot solvent quality vs. specific product components. Figure 7A (pyrite content vs. solvent quality) identifies each point by run/ material balance number and can be used as a guide to identify the equivalent run in Figures 7B-7D.

Solvent quality does not appear to affect product yield. However, the percent pyrite in the feed coal appears to affect solvent quality; that is, if the percent pyrite is below 1.1 wt %, the solvent quality value deviates from the major distribution cluster. The operating conditions during runs 206 and 207 were upset because the high-pressure separator failed and nearly 70 vol % of the unit was filled with cresol-insoluble material. Run 208, which was short, however, had the highest solvent quality (70) and lowest (1.1%) pyrite content. This solvent quality value is unusually high; its cause is unknown and only one material balance (MB) sample was taken for this run. Daily solvent qualities measured before and after the 208AB MB were between 64 and 66.

Lafayette Kentucky #9 Coal. Runs 163 to 201 were conducted with Lafayette coal. Runs 163, 166, and 201 were at 75% dissolver volume at 1,700 psi and 825°F; dissolver pressure in runs 167, 168, 171, and 172 increased to 2,100 psi with only 50 vol % of the dissolver in use; and run 190 was performed at 2,100 psi, 825°F, and 75% dissolver volume. The largest volumes of anthracene oil were added to the system between runs 170 and 182. Solvent quality increased from 65 to 75, but fell to 68 after run 182 and remained there until the next coal type (Dotiki) was used. Figures 8A-8D illustrate the relationship for Lafayette coal. Note that most Lafayette feed coals had a pyrite content of less than 1.2 wt %.

Pyro Kentucky #9 Coal. Pyro Mine coal was run under dissolver conditions of 1,700 psi and 825°F for runs 151, 159, 160, and 161, and at 2,100 psi and 825°F for run 162. These process conditions are the most constant for the coals tested. Because run 151 was conducted with Indiana V solvent and processed 3 months before run 159, run 151 can be eliminated from each solvent quality correlation. Figures 9A-9D show the relationship between Pyro coal solvent quality and product distribution. Product yield ranged widely ($\pm 8\%$), but solvent quality changed only slightly (± 2). The range of product distribution is no less than that for other coal types that experienced solvent quality changes of more than ± 10 from the average.

Fies Kentucky #9 Coal. Fies Mine coal was processed under the most varied conditions of all coal types (Note 2). Most Fies Mine coal was run at dissolver conditions of 2,100 psi, 840°F, and 75 vol %. Only three feed coals (229A, 229B, and 210AB) had a pyrite content below 1.1%. Anthracene oil was added only once, after run 210. Solvent quality was 75 and was not greatly affected (± 2). The reason for this is not clear, but the optimum activity of hydrogenated anthracene oil may be 75 ± 2 as measured by the solvent quality test. Solvent quality and product distribution for Fies Mine coal are compared in Figures 10A-10D. In general, only total gas production (depicted earlier in Figure 4) shows any apparent correlation between solvent quality and dissolver temperature: lower dissolver temperature and higher solvent quality yield the lowest gas production.

Effect of Solvent Quality on the Attainment of Liquefaction Objectives

We assume solvents are primary products of the feed coals, therefore their compositions are affected first by the coal's structure, second by processing conditions, and third by addition of external material (LSRC), control of distillate boiling point distribution, or modification by chemical means.

Once a new steady-state process condition is reached and the solvent lined out, the solvent's new properties apparently allow a different product yield distribution to be maintained. The preheater and reactor temperatures have their greatest impact on the rate of formation of primary liquefaction products that place a demand on the solvent for rapid coal dissolution and hydrogen donation.

If the solvent is returned to the front end without addition from another stream (LSRC or distillate), we can at best anticipate an apparent steady-state solvent because the feed coal is constantly changing. Most importantly, the coal's pyrite content and distribution is more variable than the organic macromolecular structure. Figure 11 shows the range in solvent quality as a function

of coal type with and without LSRC addition, independent of process conditions, for all material balance periods. Circles represent average results, and the bars define the upper and lower limits of the solvent quality.

Next, we considered only those solvent quality results obtained from material balances more than 30 days after a change in feed coal type and more than 5 days after addition of anthracene oil. All data points were averaged by coal type with respect to their pyrite concentration (Figure 12).

Figure 12 shows that the Fies, Pyro, and Indiana V coals with >1.2% pyrite generated solvents with average SQ values above 72. The trend of Fies, Pyro, and Indiana coal data clustering together and Dotiki and Lafayette coal data clustering together was also observed for nearly all average product distributions (e.g., Figures 7-11) as well as other variables not included in this report.

Measurement of Liquefaction Behavior

Based on these observations, a logical approach to defining coal-derived recycle solvent quality is to react samples of the solvent, or the modified solvent, in the microautoclave test with the daily feed coal. This solvent quality test would involve comparison of the daily microautoclave product distribution (residue, preasphaltenes, and total benzene solubles) with the product distribution for a well-maintained standard coal of the same type. The primary liquefaction activity of the solvent would be determined under hydrogen-starved, solvent-rich conditions, to mimic the slurry tanks and the rapid coal dissolution process in the preheater at $750 \pm 2^\circ\text{F}$. The secondary liquefaction activity of the solvent would be determined from a similar product distribution under hydrogen-rich conditions (2,000 psi), to quantify the sustaining hydrogen-transfer reactions in the reactor.

These two tests would be made within the same sand bath; at the same time, a third test microautoclave would be run. In this third bomb, the standard coal type would be reacted with a standard model compound solvent mixture. Together, all three results would provide internal checks on the reliability of the test (standard coal vs. standard solvent); optimum continued dissolution of process coal (feed coal vs. recycle solvent/no H_2); and optimum continued conversion to the desired product slate (feed coal vs. recycle solvent/ H_2).

Figure 13 summarize how this approach to measuring solvent quality could be used to predict liquefaction behavior of the next day's operation. Over a 3-month period in our laboratories, we have demonstrated that solvents from holding tank V178 yield different SQ values depending on whether they are tested with the feed coal that they will be slurried within the next run or a standard Indiana V coal. The greatest difference is the relative distribution of benzene solubles to preasphaltenes. Silver and Miller (11) were first to note similar coal conversion differences when using a solvent generated from Wyodak coal and reacting it with Kentucky #9 coal.

SUMMARY

The concept of quantifying solvent quality by a microautoclave test does have merit if the test is run with the same coal-type used for coal liquefaction. Correlation of the solvent quality result to preheater chemistry (rapid coal dissolution with minimum hydrogen shuttling) and reactor chemistry (rapid and sustaining hydrogen donation/shuttling) is apparently possible. As used at Wilsonville during runs 133-234, the microautoclave SQ result was of tangential significance for absolute day-to-day pilot plant operation. However, during the past 4 years the Wilsonville staff has collected SQ data under the most varied of conditions, e.g., changes in feed coal, addition of LSRC to the solvent, redefinition of solvent boiling range, and most recently, addition of hydrotreated material to the solvent. These SQ results do provide us with a relative measure of coal conversion behavior to solvent composition under pilot plant conditions to consider for future process design. The Wilsonville staff has prepared a topical report on solvent activity covering this subject (12).

From our SQ study of Wilsonville it is our opinion that bench-scale experiments comparing different coals with solvents of questionable parentage for single pass conversion are at best of limited relative value, and result in conflicting interpretations from lab to lab. Such experiments do define the kind of solvent composition that provides specific results. If such results or such solvents can be produced in situ is another question. Laboratory liquefaction experiments that may be the most meaningful (although the most time-consuming and expensive) are full recycle of the solvent for attaining apparent steady-state operation. We estimate 5-12 solvent passes are required for line-out depending on process conditions.

Note 1

Wilsonville Solvent Quality Test (#43080-60): Into a 30 mL bomb, add 1.5 g of standard Indiana V coal, 12 g of solvent, and a 1-in. steel rod. Place in sandbath (750°F) for 10 min and shake at 1,000 spm over 1.5 in. Extract the reaction products with tetrahydrofuran (THF) to determine THF insolubles. Calculate percent conversion on MAF coal. See Reference 12 for details.

Note 2

The full data base is available upon request from the author.

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FIGURE 1
WILSONVILLE PILOT PLANT PROCESS FLOW DIAGRAM

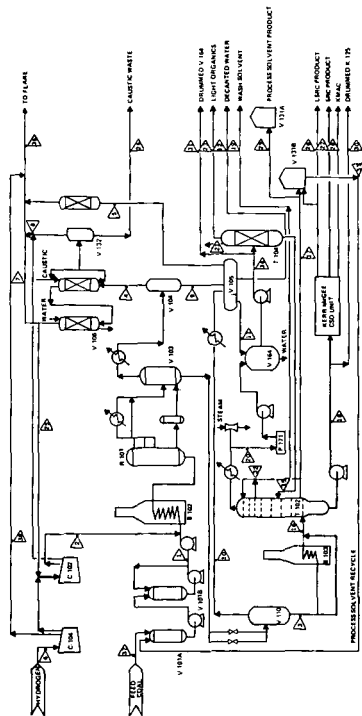


FIGURE 2
WILSONVILLE SOLVENT QUALITY (SQ)
VS.
COAL TYPE

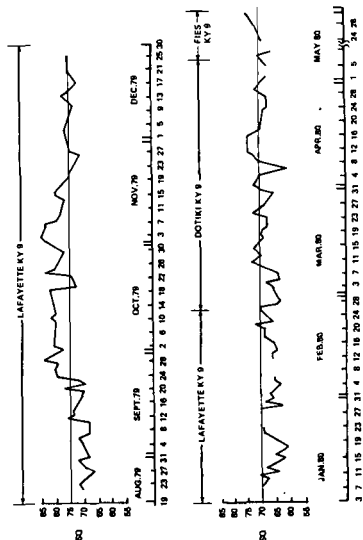


FIGURE 3
TOTAL GASES VS. SOLVENT QUALITY
ALL DATA POINTS

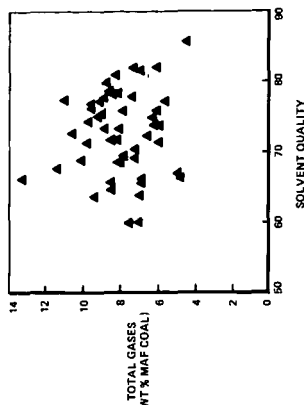


FIGURE 4
SOLVENT QUALITY VS. TOTAL GAS (WT % MAF COAL)

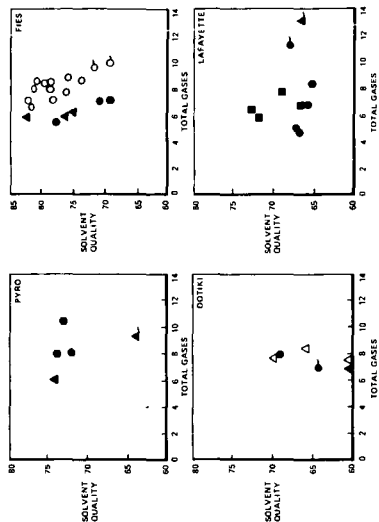


FIGURE 5
TOTAL GAS (HYDROCARBON + HETEROATOM)
AS A FUNCTION OF TIME

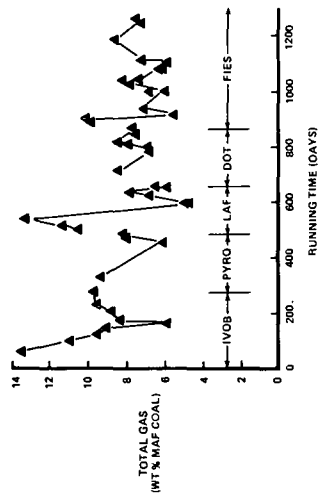


FIGURE 6
HYDROGEN CONSUMPTION VS.
TOTAL GAS PRODUCTION
ALL DATA POINTS

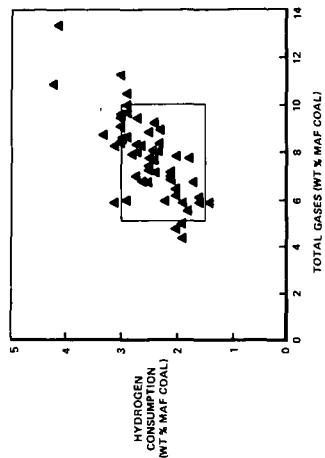


FIGURE 7

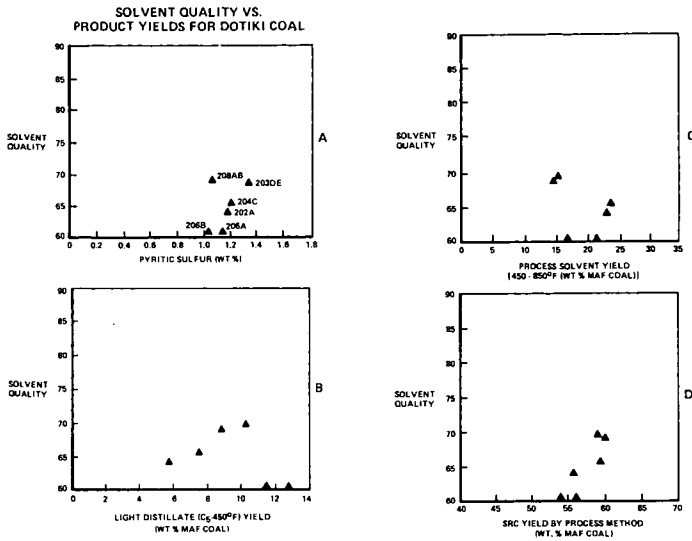


FIGURE 8

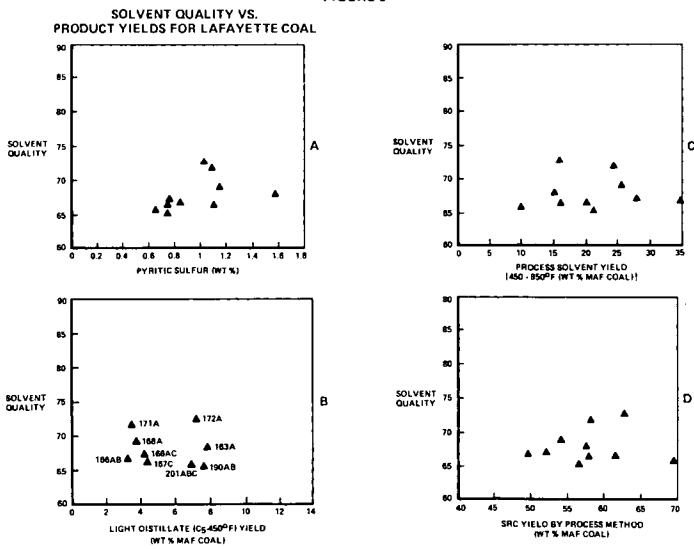


FIGURE 9

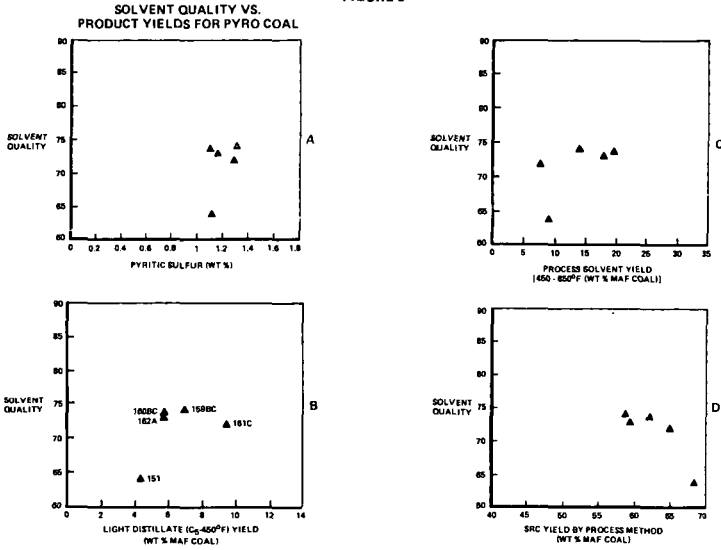


FIGURE 10

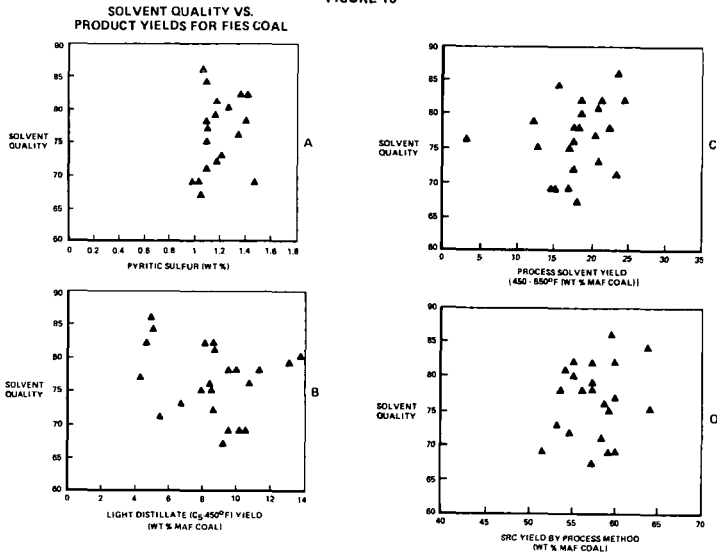


FIGURE 12
COAL PYRITE VS. SOLVENT QUALITY
BY COAL TYPE

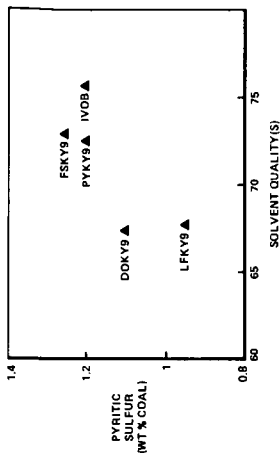


FIGURE 11
WILSONVILLE SOLVENT QUALITY (SQ)
VS. COAL TYPE

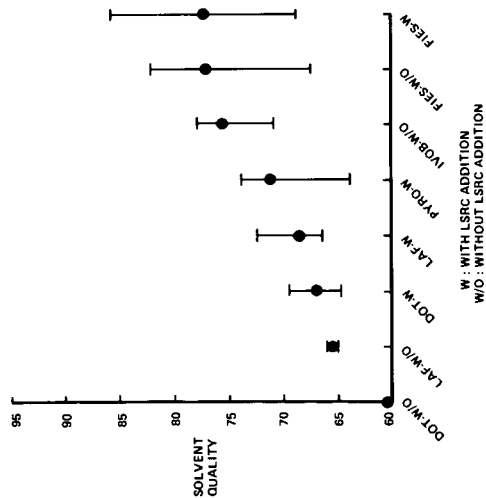


FIGURE 13
PROPOSED
SRC-I SOLVENT QUALITY TEST

COAL SOLVENT	STD SOLVENT TET/MN	DAILY RECYCLE SOLVENT	DAILY RECYCLE SOLVENT & ADDITIVE	STD PROCESS COAL-TYPE (1)	QUALITY ASSURANCE TEST	DAILY TOTE-BIN NO H ₂ (1)	DAILY TOTE-BIN H ₂ (2)
						PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT DISTRIBUTION
						PRIMARY COAL DISSOLUTION	SECONDARY PRODUCT DISTRIBUTION

- (1) MICROAULOCALVE SIC (8/1), 10 MINUTES AT 750°F
DETERMINE: RESIDUE (THP) - PREASPHALTENES - BENZENE SOLUBLES
- (2) TEST CONDITIONS TO BE DETERMINED

EFFECTS OF HEAVY RECYCLE SOLVENT COMPONENTS ON DIRECT COAL LIQUEFACTION

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Introduction

The quality of the recycle solvent is critically important in all direct coal liquefaction processes. The fact that overall solvent quality can be greatly improved by adding some of the lighter nondistillable products to the solvent is one of the most important discoveries in direct coal liquefaction research in recent years.⁽¹⁾ Many recent studies have focused on the role of solvent in direct liquefaction. It has been shown that most hydrogen transferred to the dissolving coal during initial preasphaltene formation comes from the solvent rather than hydrogen gas.^(1,2) The high molecular weight aromatic hydrocarbons in the recycle solvent are particularly adept at transferring hydrogen to coal and can retard retrogressive reactions which can lead to the formation of undesirable insoluble products. On the other hand, the coke formation reactions are also caused in large part by high molecular weight solvent components, particularly those containing phenolics and polyfunctional compounds.⁽⁴⁾

Other studies have focused on the role of nitrogen-containing aromatics in the recycle solvent. The lower molecular weight aromatics which contain basic nitrogen have been shown to be excellent hydrogen transfer agents⁽⁴⁾ and may also readily penetrate the coal structure to react with reactive coal species before retrogressive reactions can take place.⁽⁵⁾

One of the problems encountered in all of these studies has been that when actual process derived solvents are used, they are so complex that the results are hard to assign unambiguously to particular chemical properties of the solvent, while the use of model compounds have simply not included materials of sufficiently high molecular weight to adequately represent the heavier species in true recycle solvents.

The purpose of this work is to further study the liquefaction chemistry of the heavier materials in a process derived liquefaction solvent. Solvents obtained from near equilibrium operation of the Lummus ITSL Process are being used because others have shown that this solvent is less complex than solvents from other processes.⁽⁶⁾

Experimental

Samples of SCT Recycle Solvent (2SCT16-1122), the solvent recycled to the short contact time coal dissolution step, and SCT Heavy Oil Product (2SCT16-1122), the 500°F product from the same process step, were obtained from the Lummus ITSL Process pilot plant.

Both of these materials are black solids at room temperature. Analyses are listed in Table 1. Both have number average molecular weights (by vapor pressure osmometry) between 400-500 grams/mole. The SCT Heavy Oil Product, which is approximately a 1.8:1 mixture of reacted SCT Recycle Solvent and dissolved coal, has an H/C ratio of 0.80, slightly higher than the H/C ratio of the starting Illinois #6 coal and somewhat less than the H/C ratio, 0.95, of the SCT Recycle Solvent.

Illinois #6 coal used in the Lummus ITSL Process was also obtained and analyzed with the results shown in Table 2. The coal has been dried to approximately 4 percent moisture and ground to more than 70 percent -200 mesh for use in the process.

The procedure used for the liquefaction studies consists of mixing solvent and coal in a microautoclave (~18 cc volume) and pressurizing with either hydrogen or helium, containing a small amount of krypton as an internal standard, to 1000 psia (at room temperature). Standard reaction conditions are 800 F for 5 minutes. The autoclave is agitated with a wrist action shaker and heated in a fluidized sand bath. The autoclave is equipped with a thermocouple and recording pressure transducer. A typical pressure and temperature versus time curve is shown in Figure 1. The average heatup time, to 790 F, is 1.9 minutes. After reaction, quenching to 600 F requires ~0.5 minutes. This method gives excellent control of residence time at temperature.

The gases are transferred to storage in a 2-liter evacuated gas bulb for later analyses. The liquefaction products are washed from the autoclave with THF and the insolubles are extracted with THF in a Soxhlet extractor. Conversions of MAF THF insolubles are calculated using the weights of insoluble organic material (IOM) in the coal and solvent, the starting ash content of the solvent and coal and the moisture content of the coal. Excess THF is stripped from the THF solubles on a rotary evaporator and the resulting concentrated solution is slowly added to 20 parts of boiling heptane per part of THF to precipitate heptane insolubles. After the THF is distilled from the mixture, the precipitate is allowed to settle overnight and removed by vacuum filtration. The heptane is distilled from the filtrate and each of the fractions is dried in a vacuum oven overnight at 110 C, cooled and weighed. Net changes in the amounts of THF soluble-heptane insolubles (asphaltenes and preasphaltenes) and heptane solubles (oils) are calculated by subtracting blank extraction data for the starting solvent and coal to obtain differential solubility changes caused by liquefaction.

The gases are analyzed for H_2 , CO, CO_2 , CH_4 , C_2 's and Kr. After normalization to a standard krypton concentration, net yields (or losses of hydrogen) for each gas are calculated.

Results and Discussion

In order to study the chemistry of the 800°F Recycle Solvent components, the SCT Recycle Solvent was separated by vacuum distillation into fractions with boiling points above and below 800 F (427 C). Liquefaction experiments using the 800°F material serve as a baseline to allow a systematic study of the effects of addition of various fractions of the 800°F materials to the liquefaction solvent. Additional chemical insight may be obtained by running reactions in the presence and absence of a 1000 psia (cold) hydrogen atmosphere. Also, the use of the same chemical class fractions obtained from the 800°F and 800°F fractions may help illustrate the effects of higher molecular weight on the reactions of the solvent.

The SCT Recycle Solvent sample has been distilled under vacuum to obtain 800°F and 800°F fractions with the results listed in Table 3. Approximately 36 percent of the sample distilled below 800 F. The 800°F material has a higher H/C ratio and about 50 percent lower number average molecular weight. As expected, it is almost entirely heptane soluble. The 800°F fraction contains 80 percent of the nitrogen, 84 percent of the sulfur and 76 percent of the oxygen in 65 weight percent of the sample. The heteroatom concentrations are not large, however, and total only about one heteroatom per molecule (containing an average of 34 carbon atoms).

Liquefaction experiments have been done using 6 g of either the total SCT Recycle Solvent or the 800°F SCT Recycle Solvent fraction with 3 g of Illinois #6 coal under 1000 psia (room temperature) hydrogen or helium. The results are listed in Table 4.

Since both solvents and the coal are partially soluble in THF and heptane when exposed to the workup procedure before liquefaction at elevated temperature, the results have been corrected using blank extractions of the starting materials

to reflect the changes in the three solubility fractions before and after liquefaction. The results have also been corrected to remove the ash and moisture present in the starting coal. The reaction conditions have been chosen to obtain good, but not complete conversions so that differences due to the solvent and gas atmosphere can be seen. The reaction conditions gave nearly equal conversions of MAF THF insolubles, except for the 800°F SCT Recycle Solvent under hydrogen, which gave a significantly higher conversion. Most of the THF insoluble material is converted to THF soluble-heptane insolubles (preasphaltenes plus asphaltenes). Under helium there is a small net loss of heptane solubles (oils).

Hydrogen is produced on balance under a helium atmosphere while hydrogen is incorporated into the products on balance under a hydrogen atmosphere. The 800°F SCT Recycle Solvent may be exceptional in this respect and actually release a small amount of hydrogen, even in the presence of 1000 psig of hydrogen. The effects of different solvents and gas atmospheres on CO is negligible but more CO₂ is produced under helium and more CH₄ is produced under hydrogen.

The 800°F and 800°F SCT Recycle Solvent fractions are now being separated into chemical classes using the liquid chromatography method described by Later, et al.⁽⁸⁾ Preliminary results from the separation of the 800°F SCT Recycle Solvent fraction are listed in Table 5.

Table 5. Separation of 800°F SCT Recycle Solvent Fraction by Liquid Chromatography

Solvent	Chemical Class	Recovery, Weight Percent
Hexane	Aliphatic hydrocarbons	4.9
Benzene	Aromatic hydrocarbons	27.9
Chloroform	N-Aromatics	4.8
THF-EtOH (10%)	OH-Aromatics	33.3
Total recovery		70.8

The 800°F material is approximately one-quarter aromatic hydrocarbons and 5 percent of aliphatic hydrocarbons and N-aromatics.

These separations will be extended to the 800°F SCT Recycle Solvent fraction and then these fractions will be added separately to the 800°F recycle solvent to determine the effect of various types of solvent molecules on the conversion and yields during the coal dissolution step.

Acknowledgement

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TABLE 1. ANALYSES OF SCT RECYCLE SOLVENT AND
HEAVY OIL PRODUCT FROM THE LUMMUS
ITSL PROCESS PILOT PLANT

<u>Sample</u>	<u>SCT Recycle Solvent</u> (2SCT16-1122)	<u>SCT Heavy Oil Product</u> (2SCT-1122)
<u>Elemental Analyses, Wt %</u>		
Ash	1.30	3.61
Carbon	86.77	85.87
Hydrogen	6.88	5.74
Nitrogen	0.94	1.02
Sulfur	0.53	0.99
Oxygen (by difference)	3.6	2.8
H/C	0.95	0.80
<u>Distillation Data, Wt %</u>		
800°F	35.6	38.2
800°F	64.4	61.8
<u>THF Solubility, Wt %</u>	96.4	88.6
<u>Molecular Weight, g/mole</u>	477	424

TABLE 2. ANALYSES OF ILLINOIS #6 COAL FROM THE
LUMMUS ITSL PROCESS PILOT PLANT

<u>Proximate Analyses, Wt %</u>	<u>As-Received</u>	<u>Dry</u>
Moisture	3.99	-
Ash	9.72	10.12
<u>Elemental Analyses, Wt %</u>		
Carbon	69.73	72.63
Hydrogen	4.93	4.67
Nitrogen	1.18	1.23
Sulfur	2.88	3.00
Oxygen (by difference)		8.35
H/C		0.77
<u>Particle Size Distribution, Wt %</u>		
+70 mesh	0.07	
-70 +120	3.64	
-120 +200	18.90	
-200 +325	14.84	
-325	62.55	
<u>THF Solubility, Wt %</u>	13.7	

TABLE 3. ANALYSES OF 800°F AND 800°F FRACTIONS FROM
THE DISTILLATION OF SCT RECYCLE SOLVENT
(2SCT16-1122)

<u>Sample</u>	<u>800°F</u>	<u>800°F</u>
<u>Weight % of Starting Material</u>	35.6	64.4
<u>Elemental Analyses, Wt %</u>		
Carbon	90.96	87.88
Hydrogen	7.12	6.18
Nitrogen	0.57	1.30
Sulfur	0.23	0.69
Oxygen (by difference)	1.12	1.95
Ash	<0.01	2.00
H/C	0.94	0.84
<u>Molecular Weight, g/mole</u>	257	456
<u>Solubilities, Wt %</u>		
THF insolubles	0.0	5.5
Heptane insolubles	1.5	39.5
Heptane solubles	8.5	57.9

TABLE 4. SUMMARY OF MICROAUTOCLAVE LIQUEFACTION RESULTS
WITH SCT RECYCLE SOLVENTS AND ILLINOIS #6 COAL

<u>Run No.</u>	<u>7</u>	<u>15</u>	<u>9</u>	<u>17</u>
<u>Solvent</u>	<u>Total SCT Recycle Solvent</u>		<u>800°F SCT Recycle Solvent</u>	
<u>Gas Atmosphere</u>	<u>He</u>	<u>H₂</u>	<u>He</u>	<u>H₂</u>
<u>Conversion of MAF</u>				
<u>THF Insolubles, %</u>	78.2	75.0	78.6	84.6
<u>Net Change of Heptane</u>				
<u>Insolubles, % of Total</u>	19.0	17.8	18.0	19.2
<u>MAF Products</u>				
<u>Net Change of Heptane</u>				
<u>Solubles, % of Total</u>	-2.0	0.5	-0.0	1.1
<u>MAF Products</u>				
<u>Gas Analyses, Volume %</u>				
H ₂	0.85	-7.87	1.09	1.55
CO	0.16	0.12	0.13	0.14
CO ₂	1.06	0.75	1.15	0.58
CH ₄	0.77	0.98	0.75	0.90
C ₂ H ₄ /C ₂ H ₆	0.49	0.39	0.35	0.34

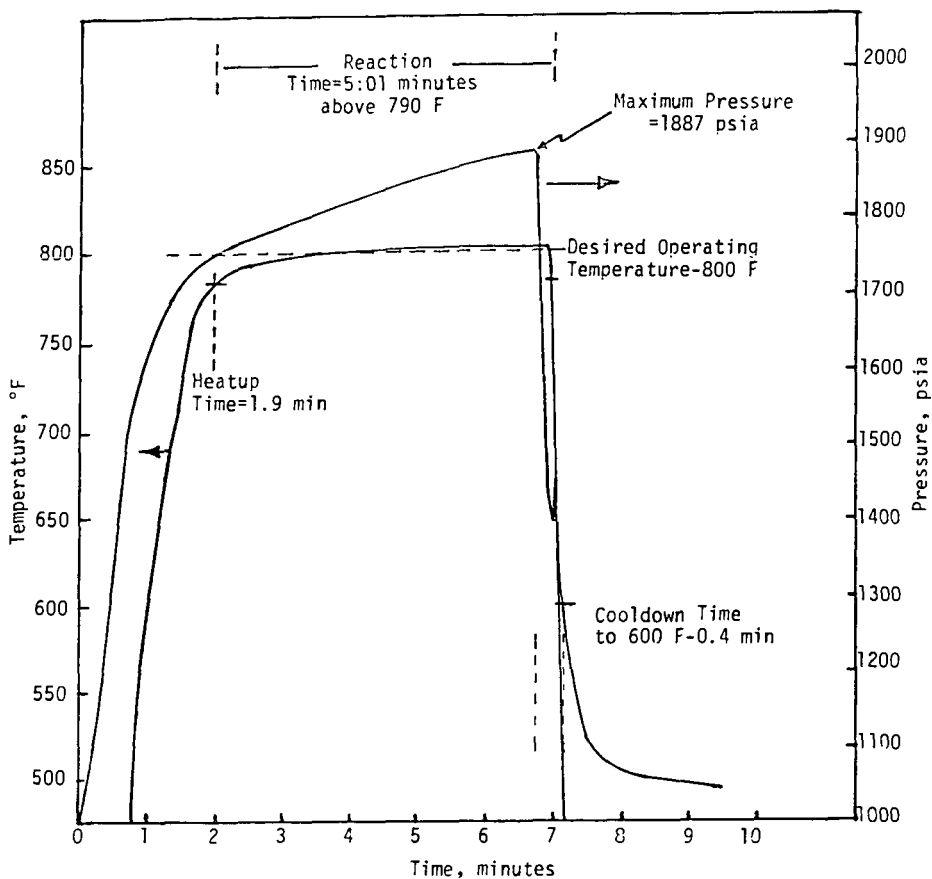


FIGURE 1. TYPICAL MICROAUTOCLAVE PRESSURE, TEMPERATURE VERSUS TIME CURVE FOR SRT COAL LIQUEFACTION

THE ORTHO-ALLYLBENZYL RADICAL: A SENSITIVE PROCEDURE FOR
THE ASSESSMENT OF HYDROGEN DONOR SOLVENT REACTIVITY.*

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The thermal conversion of coal involves the decomposition of inter-connected hydroaromatic structures into resonance stabilized benzylic radical fragments. Capping of these radicals with hydrogen from a donor solvent leads to the formation in high yields of lower molecular weight soluble and volatile products (1-5). In the absence of a donor solvent, the radicals abstract hydrogen from alkyl coal structures and depending on the supply of donatable hydrogen within the coal, conversion yields may be greatly affected (3, 6). In view of the great variety of radicals which must form during coal liquefaction and the many possible competing reactions which lead to products, the ability of a donor solvent to transfer hydrogen to coal radicals is undoubtedly of great importance.

Although much quantitative data describing the reactions of alkyl and heteroatom radicals with hydroaromatic donor solvents exists, (7-9) surprisingly little data is available on the reactions of resonance stabilized radicals with hydroaromatic donors (10-14). Realizing the importance of this data to the development of a basic understanding of coal conversion chemistry we have developed a procedure for the quantitative determination of hydrogen donor strengths toward benzyl radical. The method competes the rearrangement of o-allylbenzyl radical against hydrogen transfer to the radical from a donor solvent, see Equations 1 and 2. At this time, the method provides relative and estimated absolute rates of hydrogen atom transfer. Experiments are in progress which are designed to convert these relative rates to absolute rates with a high degree of accuracy and precision.

Experimental

Synthesis of o-allylazotoluene. o-allylbenzylazine was synthesized from o-allylbenzaldehyde and hydrazine sulfate according to the procedure of H. H. Hatt (15). The azine was reduced to its corresponding hydrazine derivative with Na-Hg(5%) in methanol. o-Allylbenzylhydrazine was oxidized to o-allylazotoluene according to the procedure of Cohen and Wang (16); m.p. 47.5-49.0°C; NMR (CDCl₃), 7.33-7.20 (sharp m, 8H, aromatic-H), 6.25-5.75 and 5.15-4.80 (m, 6-H, olefinic-H), 4.96 (s, 4-H, benzyl-H to nitrogen atom, superimposed on vinyl region), 3.48 (d of t, 4-H, J = 6.2, 1.5Hz, benzyl-H to vinyl group); Analyses: Calc., C, 82.72, H, 7.64, N, 9.65; found, C, 82.6, H, 7.73, N, 9.58.

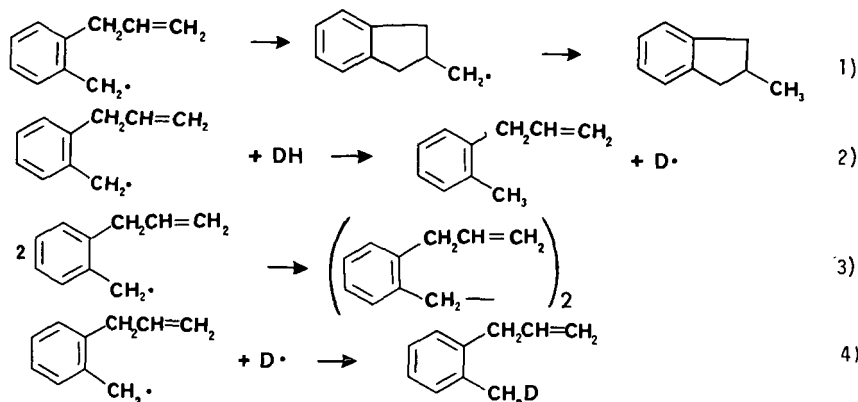
Determination of relative rates of hydrogen atom transfer to o-allylbenzyl radical. Solutions of the o-allylazotoluene, hydrogen donor, and sometimes an inert solvent such as benzene or phenyl ether, were degassed and sealed in pyrex tubes and then thermostatted for 20 minutes (approximately 2 half-lives). The concentration of azo compound was kept low (<.01M) to minimize radical induced decomposition and to minimize consumption of donor solvent (usually <5% consumed). The relative amounts of 2-methylindan (2MI) and

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and o-allyltoluene (OAT) were determined by capillary gas chromatography analysis after they were separated from the unreacted azo compound by high performance liquid chromatography. In calculating k_{abs}/k_{re} , the room temperature concentrations of donor solvents were corrected to reflect the solution density at 160°C (17). We expect the error in these values to be $\pm 5\%$ due to lack of precise information about the actual liquid densities.

Results and Discussion

o-Allylazotoluene is a conveniently prepared thermal source of o-allylbenzyl radicals. In donor solvents equivalent to or better than m-xylene it has a half-life of approximately 10 min at 160°C. Upon decomposition, a pair of o-allylbenzyl radicals form and undergo reactions of rearrangement, hydrogen abstraction and combination.



The yields of products, 2-methylindan (2MI), and o-allyltoluene (OAT), formed from the competing reactions of rearrangement, Equation 1 and hydrogen atom abstraction, Equation 2, are observed to vary according to the hydrogen donor strength of the donor solvent (DH). Under the experimental conditions, the formation of 2MI and OAT are irreversible and the amount of DH consumed is small, so that the rate constant for hydrogen abstraction, k_{abs} , relative to rearrangement, k_{re} , for a given donor is provided by the expression,

$$\frac{k_{abs}}{k_{re}} = \frac{[OAT]}{[2MI][DH]n} \quad (5)$$

where n is the number of donatable hydrogens per donor molecule.

The formation of 2MI is controlled by the unimolecular rearrangement of o-allylbenzyl and the rate constant, k_{re} , for this reaction is independent of solvent composition, such that the values, k_{abs}/k_{re} , provide a quantitative index of hydrogen donor strength. In Table I, index values for a series of hydrogen donor solvents and model compounds have been compiled from k_{abs}/k_{re} values. For convenience of comparison, the values have been indexed relative to m-xylene for which k_{abs}/k_{re} is 2.53×10^{-3} .

Interestingly the index quantitatively bears out the expected relationship between donor strength and resonance stabilization energy of the radical formed from the donor molecule, i.e., 9,10-dihydroanthracene > allylbenzene > 9,10-dihydrophenanthrene > diphenylmethane > m-xylene. Diphenylmethane is

a much poorer solvent than dihydroanthracene because steric hinderance prevents both phenyl rings from being simultaneously conjugated with the radical site. Little steric hinderance is in effect for the radical derived from allylbenzene and therefore the radical experiences greater resonance stabilization than diphenylmethyl radical and exhibits a greater rate of hydrogen donation. Of the recyclable solvents, 9,10-dihydroanthracene is a far superior donor to tetralin or 9,10-dihydrophenanthrene.

The index quantitatively illustrates the astonishing effects of combined polar and resonance effects in accelerating atom transfer reactions, i.e., thiophenol > phenol > xylene. These results indicate that compounds such as naphthols and thiols are among the most important donors in high sulfur coals and oxygen rich medium ranked coals. It is clear that they play important and as yet relatively unknown roles in the formation of soluble conversion products and chars (18).

These results easily show the importance of establishing such a method for assessing donor solvent strengths. Furthermore, good methods for estimating the Arrhenius parameters for the absolute rate of rearrangement for o-allylbenzyl radical are at hand (19) and an experimental determination is in progress. Therefore, this body of data will be of great value both to researchers involved in developing thermochemical kinetic models of coal liquefaction and to investigators interested in understanding basic chemical transformations.

Table I. Hydrogen Donor Strength of Selected Solvents and Model Compounds Towards o-Allylbenzyl Radical.

Donor	Relative Donor Strength
m-xylene(a)	1
1,5-Cyclooctadiene	11
Diphenylmethane	20
Tetralin	27
9,10-Dihydrophenanthrene	33
Phenol	76
Allylbenzene	114
9,10-Dihydroanthracene	635
Tri-n-butylstannane	3.2×10^5
1-Naphthol	1970
Thiophenol	1.10×10^6

(a) $k_{abs}/k_{cyc} = 2.53 \times 10^{-3}$

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THE USE OF o-TERPHENYL AND DIBENZO(c,g)PHENANTHRENE
TO STUDY H-DONOR SOLVENTS

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The use of H-donors to increase yields of distillable liquids in direct coal liquefaction is well-documented (1,2,3). Several mechanisms have been proposed including the radical-trapping of hydrogen from the H-donors (4,5). Another mechanism suggested on the basis of thermochemical data (6) is a transfer of a hydrogen atom (radical) to an aromatic compound. This transfer is energetically favorable when specific atoms in the aromatic molecule are attacked. Phenanthrene, for example, is stabilized by 38 kcal/mole when attacked by a hydrogen radical to form the 9-hydro-phenanthryl radical. This addition of hydrogen has not been studied to any extent at either of the model compound level or the process level.

Another reaction which may resemble the radical addition reaction was observed when 1,1'-binaphthyl was heated with an H-donor to form the thermally stable perylene (PER) (7). An H-donor was essential for coupling and different H-donors produced perylene in different yields. This reaction was used to study the relative ability of an H-donor to transfer its hydrogens at the high temperatures and pressures used in liquefaction. The coupling reaction appeared to have potential as a system to study this variety of H-transfer which may have important implications in the direct coal liquefaction process.

Problems encountered in this method of evaluating H-donors included the low yields of perylene and the low solubility of perylene in many solvents. Molar ratios of perylene to starting materials ranged from 1×10^{-2} to 28×10^{-2} after 1 hour reaction at 470°C. It was thought that a higher conversion of substrate would improve the reliability of the analytical method and would allow for shorter reaction times. One solution to the problem connected with the coupling to form perylene would be to find another molecule which would react by a similar mechanism but would give higher yields of a thermally stable product under similar reaction conditions. Copeland, Dean, and McNiel (8) reported that o-terphenyl (OTP) gave higher (60 pct) yields of coupled product, triphenylene (TP), than binaphthyl (18.7 pct) gave perylene when reacted with decalin at 490°C with a catalyst and hydrogen for 3 hours. Triphenylene was very stable and this reaction appeared to be a good alternative candidate for evaluation of H-donor reactivities. Several reactions were carried out with the o-terphenyl (Wiley Organics) and various H-donors at 470°C for 1 hour without hydrogen gas in small microreaction vessels. The results of these reactions are summarized in Table I and are compared to previously obtained results with 1,1'-binaphthyl (7).

TABLE I

MOLAR RATIOS OF PRODUCT OF REACTANT FOR REACTIONS OF o-TERPHENYL
AND 1,1'-BINAPHTHYL WITH H-DONORS AT 470°C FOR 1 HOUR*

H-Donor	TP/OTP x 10 ⁻²	PER/BN x 10 ⁻²
9,10-dihydrophenanthrene	2.05	3.1
1,2-dihydronaphthalene	2.47	3.4
1,2,3,4-tetrahydronaphthalene	2.51	1.3
fluorene	5.91	2.0
4,5-dihdropyrene	1.65	14.1
1,2,3,6,7,8-hexhydropyrene	--	28.0
indane	0.42	1.27
1,2,3,4-tetrahydroquinoline	0.37	--
1,2,3,4-tetrahydroisoquinoline	0.40	1.38
2,3-cyclohexenepyrindine	0.88	--
indoline	--	3.84
5-indanol	0.49	1.24
indene	1.92	3.19

*Obtained by (Mole % coupled product)/(Mole % starting OTP or BN + sum of mole % of by-products)

The ratios of coupled product to starting materials were less satisfactory than those of binaphthyl in predicting H-donor ability. Some H-donors which promoted higher yields of perylene from binaphthyl also produced higher yields of triphenylene from o-terphenyl. There were exceptions including fluorene, 4,5-dihdropyrene and 1,2,3,6,7,8-hexhydropyrene which gave differing amounts of coupled product and in some cases even gave opposing trends. It was found with both substrates that many H-donors known to be good donors at lower temperatures did not give significant amounts of coupling at the higher temperatures used. This was particularly true of the heteroaromatic compounds with hydrogen attached to the heteroatom such as with 1,2,3,4-tetrahydroquinoline.

The conversion of o-terphenyl to triphenylene was not as great as expected based upon the three-fold yield of triphenylene over perylene (Equation 1). Moreover, very close to the peak of triphenylene in the gas chromatogram (using 6' x 2 mm ID 3 pct Dexsil 300 on Supelcoport 100/120 with programmed temperature) were several peaks analyzed by GCMS to be quatraphenyls (MW 306). Large amounts of biphenyl from the cracking of the terphenyl also reduced the possible yield of triphenylene and this complicated the analysis and the possible implications of the reactions to liquefactions.

Kinetics of the conversion of o-terphenyl to triphenylene were studied and compared with previous results of conversion of 1,1'-binaphthyl to perylene under similar conditions. The results are summarized in Table II.

TABLE II

PSEUDO FIRST ORDER RATE CONSTANTS FROM THE CONVERSIONS OF o-TERPHENYL
AND 1,1'-BINAPHTHYL TO TRIPHENYLENE AND PERYLENE RESPECTIVELY

H-Donor	o-Terphenyl (k, min ⁻¹)	1,1'-Binaphthyl (k, min ⁻¹)
9,10-dihydrophenanthrene	7.0×10^{-3}	1.2×10^{-2}
1,2,3,4-tetrahydronaphthalene	7.4×10^{-3}	1.9×10^{-2}
1,2-dihydronaphthalene	---	---

The similarity between the products and the similar rate constants for each H-donor implied that the same mechanism was involved. When modeled as a first order reaction (Table II), o-terphenyl conversion was slower than binaphthyl conversion. It was interesting that 1,2-dihydronaphthalene formed no more coupled product with either binaphthyl or o-terphenyl after 45 minutes substantiating a similarity in the mechanism. The lower rate constants and the extra side products formed with o-terphenyl led to the conclusion that this system was less advantageous binaphthyl than coupling in the study of H-donor solvents.

Dibenzo(c,g)phenanthrene (DBP) (Equation 1) was investigated as another substrate likely to be a substitute for o-terphenyl and binaphthyl. Its structure suggested the possibility of facile coupling which could lead to enhanced rates and greater yields of coupled products. Dibenzophenanthrene was synthesized by coupling 1-tetralone to bis-dialin (BD) which was then reacted with maleic anhydride (9,10). The adduct was then brominated, dehydrobrominated, decarboxylated, and finally dehydrogenated to the desired dibenzo(c,g)phenanthrene, (Equation 1).

The low yield (7.5% overall) of dibenzophenanthrene was quite poor compared to that in the synthesis of binaphthyl (60%) from the common intermediate, 1,1'-dialin. The final product separated on an alumina chromatographic column with petroleum ether was 89% (VPC) pure. A small amount of this compound was reacted with 9,10-dihydrophenanthrene in the microreactor under the usual conditions. The yield of 8% coupled benzo(1,12)perylene (BP) product was an order of magnitude larger than either triphenylene or perylene. The retention time of the coupled product, benzoperylene, of 20.5 minutes was significantly longer than the retention times of other peaks in this reaction or of any component found in hydrogenated anthracene oil used as an experimental H-donor. There appeared to be no side reactions except some transfer of hydrogen from H-donor to the dibenzophenanthrene. Thus preliminary results indicate dibenzophenanthrene might have distinct advantages over binaphthyl or o-terphenyl and would provide a very promising system to apply to the study of H-transfer reactions.

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